Research Proposal

Proposed Title of Work: *Computational Exploration on the Electronic Structure and Functionalities of some Organic Frameworks*

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Table of Contents

Sl. No.	Topics	Page No.
1	Origin of the research problem	2
2	Objective of the work	3
3	Methodology	4
4	Future Prospect	6
5	References	7

(a) Origin of the research problem

Nowadays, two-dimensional materials have attracted much attention due to their extraordinary properties and effective applications. Graphene,[1-3] discovered by Andre Geim and Konstantin Novoselov, is a well-known 2D material because of its high specific surface area, excellent charge carrier mobility, superior electrical conductivity, and outstanding mechanical properties [4] etc. However, graphene is a gapless semiconductor [5], which is major headache to use it in nanoscale electronics. To open the band gap, methods of reduction of dimensionalities have been applied but it occurs at the cost of huge decrease in electron mobility. The field of graphene is now on the way of saturation and search for new exciting 2D materials lead us to metal-organic frameworks (MOFs) [6] and covalent-organic frameworks (COFs) [7]. Although both MOFs and COFs are crystalline porous materials with high surface area, adjustable pore size and tunable internal chemical environment, COFs have some unique features such as low mass density, high thermal stability, and chemical stability. COFs are an emerging class of crystalline porous 2D or 3D materials in which the organic building blocks are integrated into an ordered structure with atomic level precision and predictable control over composition, topology, and porosity.

COFs are usually composed of light weight elements such as B, C, N, H and O, resulting in low mass density. The building subunits of COFs are linked by strong covalent bonds, imposing COFs with high thermal stability. COFs are basically synthesized via reversible covalent-bond-forming reactions such as condensations. Varoius synthetic methods are employed to develop COFs, namely, solvothermal synthesis, ionothermal synthesis, microwave synthesis etc. The diversities of organic synthetic reactions and organic building blocks lead to design and synthesize COFs with specific functions and structures [8-14].

Due to high surface area and permanent porosity COFs have been emerged as potential candidates for gas storage applications. The property of tunable pore size of COFs has been utilized for gas seperation [15-20]. Computational studies on some 2D COFs indicate a large electronic coupling between the π-orbitals of the stacking layers which facilitates the transport of charge carriers and excitons, giving rise to the semiconducting, optoelectronic and photoconductive nature. The optical properties of COFs can be tuned by changing the organic building subunits which make them facile to be used in photovoltaic and light-emission devices. The wide range of exciting properties of COFs lead them to be used in many applications such as catalysis, energy storage, large

molecule uptake, sensors etc [21-23].

(b) Objective of the work

Recently, Huang et al. [24] have reported a thiophene-containing covalent triazine framework (TBCTF) as a photocatalyst for metal free, visible-light promoted selective oxidation of alcohols into the corresponding aldehydes and ketones, using molecular oxygen as a clean oxidant at room temperature. This is constructed by a donor (D) moiety thiophene and an acceptor (A) unit triazine. The donor–acceptor heterojunction is an important key structure in current technologies, including light-emitting diodes, transistors, and photovoltaics, because it controls the charge dynamics in the devices. In this context, we want to carry out a theoretical study using density functional theory (DFT) calculations on the electronic properties of TBCTF. We would like to investigate its photovolatic application by charge separation between donor-acceptor moiety. We are interested to show how to tune its charge separation property by suitable pairing of different donor and acceptor moiety for application in optoelectronic devices. We will carry out the modification of organic building blocks (thiophene & triazine) [25,26] and introduce electric field to the aim of band gap engineering. COFs have been synthesised in layered form and we wish to investigate the electronic properties of this bilayer TBCTF. In this bilayer TBCTF, we want to observe how the electronic properties change with variation of interlayer distance, that is we want to impose strain along z-direction. Mainly, COFs are spin-unpolarized so its applicationin spintronic devices are restricted [27] , hence we are interested to find out the way of generating spin-polarization in TBCTF and want to systematically calculate its spin related electronic and magnetic properties. Recently, Wang et al. Have designed a graphitic zinc oxide based intrinsic type-II heterostructure, g-ZnO/blue phosphorous (BP), based on first principle calculations. The type-II band offsets and large built in electric field from BP to g-ZnO ensure the photogenerated electrons to migrate from g-ZnO to BP, which causes effective carrier seperation. We will try to composite g-ZnO with TBCTF COF and see whether this composite system can be a better candidate for photovoltaic application. We will design two composite systems namely TBCTF-TCNQ (TCNQ = Tetracyanoquinodimethane) and TBCTF-TCNE (TCNE = Tetracyanoethylene) [28-30] and would like to find out whether there is any spatially charge seperation between TBCTF and TCNQ (or TCNE). This may give rise the composite system as a suitable candidate for photovoltaic application. We wish to introduce some transition metal atoms [31] between the two layers of bilayer TBCTF and investigate how transition metal atoms affect the electronic structure of it. We have also planned to intercalate Li atom above and below TBCTF monolayer and try to understand its hydrogen

adsorption property.

(c) Methodology

The ultimate goal in Solid state Physics is to solve Schrödinger equation-

$$\hat{H}\Psi(r;R) = E\Psi(r;R) \qquad ...(1)$$

Where,

$$H = \underbrace{-\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2}_{T_e} \underbrace{-\sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2}_{T_N} \underbrace{-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}}}_{V_{eN}} + \underbrace{\sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}}}_{V_{ee}} + \underbrace{\sum_{A=1}^{M-1}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}}_{V_{NN}} \qquad \textbf{(1)}$$

Where

$$\nabla_i^2 = \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right)$$

M_A = Mass of nucleus A

Z_A = Atomic number of nucleus A

T_e = Kinetic energy operator for the electron

T_N = Kinetic energy operator for the nuclei

V_{eN} = Operator for potential energy of the attractions between the electrons and the nuclei

V_{ee} = Potential energy of repulsions between the electrons

V_{NN} = Operator considering potential energy of repulsions between the nuclei A and B

Equation (1) is impossible to solve in practice for the above Hamiltonian due to presence of cross terms r_{iA}, r_{ij}, R_{AB}. Hence approximation is required.

Born-Oppenheimer approximation:

The nuclei are much heavier than electrons (m proton =1836m e), hence they move much more slowly and can be considered frozen in a single arrangement (molecular conformation). So the electrons can respond almost instantaneously to any change in the nuclear position. Thus, the electrons in a molecule are moving in the field of fixed nuclei. So the term T N can be neglected and the molecular Hamiltonian becomes-

$$H = \underbrace{-\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2}_{T_e} \cancel{\underbrace{-\sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2}_{T_N}} \underbrace{-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}}}_{V_{eN}} + \underbrace{\sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}}}_{V_{ee}} + \underbrace{\sum_{A=1}^{M-1}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}}_{V_{NN}}$$

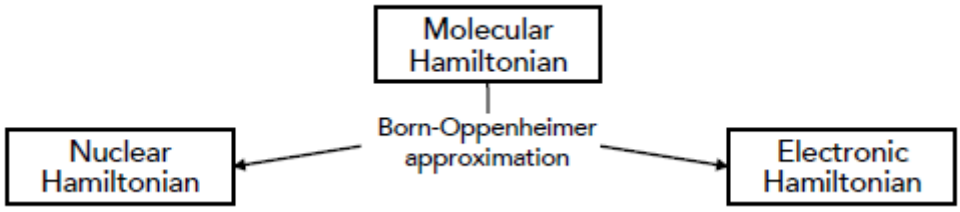
neglected

constant term

.....(2)

The Born-Oppenheimer approximation allows the total wave function to be written as product of electronic and nuclear wave function as follows -

$$\Psi(r, R) = \Psi_e(r;R) \bullet \chi_N(R)$$



Electronic Hamiltonian describes the motion of N electrons in the field of the M fixed point charges (nuclei).

$$H_e(\mathbf{R}) = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{1}{r_{ij}} \qquad \mathbf{(2)}$$

Electronic Schrödinger equation:

$$\hat{H}_e \Psi(r;R) = E_e \Psi(r;R) \qquad .....(3)$$

Solution of equation (3) gives the electronic energy E_e and the wave function $\Psi(r;R)$ for a particular value of R.

Finally total energy can be obtained by adding internuclear repulsion energy (V_{NN}) to electronic energy.

Total energy:

$$E_{tot}^{pot}(\mathbf{R}) = E_e + \sum_{A=1}^{M-1}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}$$

Equation (3) can be solved with thhelp of Density Functional Theory (DFT). The spin-polarised DFT is employed in our electronic structure calculations as implemented in SIESTA code [32]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange-correlation functional [33] is adopted with the norm-conserving pseudopotentials and the double zeta pluspolarisation basis set.

(d) Future Prospect

In this research work we will try to explore some of the interesting features of some porous organic frameworks. Our study will explore few possibilities of understanding to the experimentalists and further exploration of designing other porous organic frameworks. These organic frameworks may find application in optoelectronic and photovoltaic devices. Further these porous frameworks may also find application in gas storage, gas seperation, catalysis, and sensing etc.

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